

**THE USE OF DIETHANOLAMINE AS A CO₂ ABSORBENT IN WAS TAKE THE DETERMINATION CORAL REEF AGE IN BARRANG LOMPO ISLAND SPERMONDE ISLANDS THROUGH MEASUREMENTS OF ¹⁴C ACTIVITY BY LIQUID SCINTILLATION COUNTING (LSC) METHOD***Jumianti Bunga Matande*, Muhammad Zakir and Alfian Noor*Radiation Chemistry laboratory, Science Faculty, University Hasanuddin,
Campus UNHAS Tamalanrea Makassar, 90245**Corresponding author: chemistryjbmanti@gmail.com, Mobile: +62085 396 934 171***ABSTRACT**

Research on the use of diethanolamine (DEA) as a CO₂ absorbent in was take the determination coral reef age in Barrang Lompo Island, Spermonde Islands through measurements of ¹⁴C activity by *liquid scintillation Counting method* (LSC) was carried out. Coral reef sample of the island Barrang Lompo at coordinates 5 ° 06 '49 " LS 119 ° 25' 20" BT with a dept of 3-4 meters from the sea surface. Coral reefs (coral reef) is an ecosystem that live on the water in the form of limestone formations (CaCO₃). Sample preparation is done physically and chemically. Chemical preparation of coral reef sample was using 30% H₂O₂ continued with HClO₄ mixture and H₂O₂ 30% and the last with a solution of HCl to produce a clean sample with a weight reduction of 16.318%. Carbonate samples separated as CO₂ by reaction with 10% HCl and absorption by diethanolamine to produce carbamate compounds with 62.236% efficiency. Total carbon in the sample solution is obtained through a 1,709 gram reduction methods before and after absorption. Radiocarbon dating method is based on measuring the specific activity of the samples obtained from the results of the count Liquid Scintillation Counting (LSC) Hidex 300 SL, which is 7.938192 dpm/gC. The specific activity of the age of the coral reefs are estimated 5425.452 year.

Keywords: Spermonde, Barrang Lompo, Coral, *Liquid Scintillation Counting* (LSC), radiocarbon dating.

1. INTRODUCTION

Indonesia is one of country that has a largest sea, with an area of see more than 75%, which is 5.8 million square kilometers [8]. The sea of Indonesia is rich by marine biological resources, which is containing more than 400 coral reef species [6].

Spermonde Island is one of Indonesia's richest sources of biodiversity that is at coordinates 4 27'00 " - 5 29'00 " latitude and 119 2'00 " - 119 33'00 " BT. This position shows this island in south Strait of Makassar or on the southwestern side of the peninsula South Sulawesi (Spermonde Shelf), regardless of Shoal

Sunda. Spermonde exposure width of the mainland (mainland) towards the West about 40 kilometers with a maximum depth of 60 meters [2].

Spermonde Islands is known by many islands people as an island sangkarang consisting of ± 121 islands. As had noted by Moll (1983), in these islands have coral diversity levels were quite high because there are 78 genera and sub-genera, with a total of 262 species [10].

Coral reef has a very big role, because the coral reef ecosystem directly affects the entire life at sea and the beach in the region. Coral reefs are formed of limestone CaCO₃, has many benefits primarily as a place to live, where the



development of marine life, feeding (feeding ground), where the rearing and growth (nursery grounds) and spawning (spawning ground) for a variety of marine life. Beside of that the important coral reefs as coastal protection from degradation and abrasion and can record all the activities, habits or behavior of earthquakes in the past to determine its age^[1].

Determination of the age of the coral reefs in the waters has a big benefits in the geography learning source for example to trace and learn the formation stone shaping in the beach and is also used to determine the age radiocarbon surface water real^[12].

Reefs age can be determined by the method of radiocarbon dating. Dates based on the existence of carbon isotope (carbon-14) contained in living organisms that will dissolve when these organisms died with a half-life of 5730 years^[3].

Radiocarbon dating method is a calculation method based on the calculating activity ^{14}C that is still contained in a sample. Values obtained from the calculation of ^{14}C activity is then converted to the age after it is compared with the standard. Broadly analysis process ^{14}C that at the sample of the example preparation, sample census, the estimated sample ^{14}C activity, age determination of samples and reporting of age of the sample^[9].

Enumeration is done through a method of LSC (Liquid Scintillation Counting), samples containing radionuclides dissolved or suspended in a solution of scintillator (cocktail) that fits inside the glass or plastic vial. Radioactive particles in the sample is dissolved in a solution of scintillator will grow with molecules of the solvent causes the solvent molecules become excited and this causes

the scintillator molecules emit photons. The photon will be detected by the PMT so that the resulting electrical pulses proportional to the energy of radioactive particles^[11].

Amine compounds are most often used as an absorbent in the absorption of CO_2 is an alkanolamine compound. Alkanolamine compounds classified into 3 groups: primary amines (eg MEA), secondary amines (DEA) and the tertiary amine (TEA)^[4]. Based on research conducted by Rahmaniah (2014) and Kim et al. (2013), states that one of the amine compound ever tested that DEA is more effectively used as absorbents when compared with the MEA and TEA because it has a CO_2 absorption efficiency is greater.

2. METHODS

Tool

The tools are used in this study include: glass tools commonly used in the laboratory, erlemeyer, beaker glass, petri dish, pumpkin spray, burette, pipette scale, pipette volume, pipette, flask, beakers, bulb, stirrer, hotplate, a suite of tools absorption, impinger, absorption column, count tool LSC Hidex 300 SL, vial scintillator, Ruler, stative, mortal, gloves, baskets, oven and hammer.

Material

The materials are used in this study are: 10% HCl, 6 N HCl, 1 N NaOH, diethanolamine (DEA) 30%, HClO_4 1 N, 30% H_2O_2 , AgNO_3 0.5 M, Marble as background material, silica gel, HP N_2 gas, coral reefs, Aqualight scintillator, filter paper, aluminum foil, tissue and aquades.

Time and Place of Research

This study was implemented starting in May 2016 in the Radiation Chemistry Laboratory Chemistry Department, Faculty of Mathematics and Natural Sciences University of Hasanuddin.

Research procedure

Sampling Coral Reef

Sampling is done is Island Barrang Lompo, District Ujung Tanah, Spermonde Islands, Makassar at coordinates 5 ° 06 '49 "latitude 119 ° 25' 20" East.

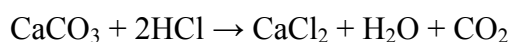
Samples laundering Coral Reef

Laundering is an early stage in the preparation of the sample before destruction or separation carbonate samples.

- a. Physical washing (washing Early Stage)
- b. Chemical washing (washing Phase Two)

Sample pretreatment Coral Reef

Each piece of dry coral reef that had weighed, crushed with a mortar up into a fine powder. For the preparation of the analysis of the content of ^{14}C in the sample, prepared the sample container filled with 40 grams of sample and reacted with HCl 10% up calcium carbonate completely reacted. In these reactions will be generated CO_2 through the following reaction:



N_2 Gas High Purity (HP) supplied to the CO_2 absorption suite of tools. CO_2 gas is then channeled to the impinger containing absorbent alkanolamine is Diethanolamine (DEA), while continuing to N_2 gas flowed HP.

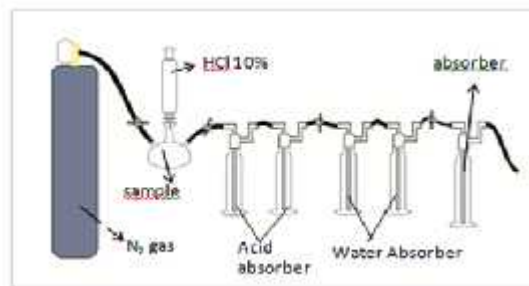


Figure 1. Design Tool CO_2 absorption of samples of coral reefs

During the absorption process, there will be hot. After a saturated aqueous solution reached temperature gradually decreases to return to room temperature. After the absorption process is complete, the solution formed is included in the 20 mL glass vial and added scintillator. Schema tool CO_2 absorption of samples of coral reefs can be seen in Figure 1. The solutions before and after the absorption process is weighed to determine the mass change is happening.

Sample enumeration Coral Reef

Sample enumeration by adding 2 ml of the sample into a vial containing 15 ml of scintillator and then shaken until homogeneous. Then the sample is enumerated with the LSC Hidex 300 SL for 24 hours with five repetitions.

Data analysis

Measurement

The tool calibrated using calibration standard solutions tools work according to instructions until later showed that the instrument has been calibrated with out the printing (system normalized). ^{14}C standard solution cassetteholder are set out in accordance with the serial numbers listed above then chopped vial following the instructions of the existing work on the tool. Filled measuring conditions in

accordance with the instructions on the appliance. Vial that had contained a homogeneous solution scintillator and sample inserted into the cassette holder and placed in a position of enumeration. Old enumeration arranged in advance that for 24 hours. START button is pressed and wait until the enumeration is completed and the results will be printed on paper (print out).

Absolute Age Calculation

Age calculation coral reefs done using the following formula:

$$t = \frac{t_{1/2} \ln \frac{A_0}{A}}{\ln 2}$$

Information :

A = radioactivity isotope ^{14}C in the sample

A_0 = radioactivity isotope ^{14}C at the time of the plant or animal life (15.3 dpm / gC) (Libby, 1960)

$t_{1/2}$ = half-life = 5730 years

$\ln 2 = 0.693$

3. RESULTS AND DISCUSSION

Sampling

Sampling was carried out on the island of coral reefs (Figure 2) Barrang Lompo Spermonde Islands at a depth of 3-4 meters from the sea surface with the aid of SCUBA divers.

Lompo Barrang Island is one of a cluster of islands in the Spermonde was administratively located in District Ungu Tanah Makassar South Sulawesi province with an area of 19 hectares.

Samples laundering Coral Reef

Washing the sample is done in two stages, the physical and chemical washing. In this way the natural contamination

found in samples of coral reefs can be eliminated, thus resulting corals appear white due to the loss of impurities and carbon source on the sample surface. Impurities are missing can be determined by calculating the difference between the dry weight of the sample before and after washing and loss of impurities at 16, 318% as shown in Table 1.



Figure 2. Sample of coral reef

Table 1. Data reef weight ratio Barrang Lompo Island Spermonde Islands before and after the washing process.

Sample	Weight Before Laundering (g)	Weight After Laundering (g)	% Weight Samples Missing
Coral reef	34.417	28.801	16.318

The washing process of washing the sample consisted of physical and chemical leaching have different functions. At the physical washing, samples of coral reefs washed using running water and flushing is done with aquades, this washing is able to remove stains or impurities that are easily lost attached to the surface of coral reefs such as soil and mud. While the chemical leaching process which starts from soaking the samples in a mixture (1: 1) 30% H_2O_2 and NaOH 1 N and



ultrasonic for 10 minutes, was able to eliminate stains attached to the narrowest impeccably reefs. Samples of coral reefs ultrasonic to accelerate the washing process by giving vibrations to the base and walls of the sample container during the washing process takes place, while soaking the samples in a mixture of acid-base second (1: 1) H₂O₂ 30% and HClO₄ 1 N capable of removing residual organic stains that brown/yellow stick coral polyps that cannot be lost on the first immersion. Perchloric acid use in the second immersion can dissolve 5-10% of the sample weight Adkins (2002). It is therefore only done soaking of about 2 minutes.

The last process in the chemical leaching is a sample immersed in 10 mL of 6 N HCl for ± 30 seconds. Soaking is done to reduce the CO₂ absorbent modern adsorbed on the surface of the sample during the washing process.

Pre-treatment Sample.

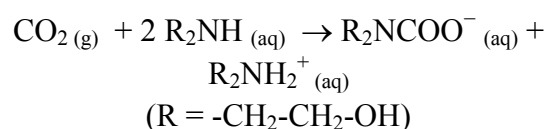
The main arranging reef is a carbonate. Carbonates found on coral reefs can be separated by reacting with HCl 10% in 5 grams of powder samples in a round-bottom flask. The sample used in the form of a fine powder obtained by grinding using a mortar. The form of these samples resulted contact space between HCl 10% with the sample becomes more widespread and the reaction that occurs can be fast. When samples of coral reefs reacted with HCl 10% will generate CO₂ gas. The reaction that occurs between calcium carbonate and hydrochloric acid are as follows:



The next process is CO₂ gas flow through the tube impinger contains filter paper that has been poured AgNO₃,

intended to adsorb excess acid produced during the reaction between CaCO₃ and HCl 10% occurred, while the silica gel in the next impinger tube serves to adsorb excess water.

In the absorption column, gas CO₂ will be absorbed by Diethanolamine (DEA). Diethanolamine which is a secondary amine compound will react absorb gas CO₂ produces carbamate compounds. In this process, not all the CO₂ gas that flowed into the solution Diethanolamine capable arrested characterized by the CO₂ gas bubbles that pass through the surface of the absorbent solution. The reaction is as follows:



Carbamate compounds that are formed will be measured by *Liquid Scintillation Counting* (LSC), is aims to determine the amount of activity ¹⁴C. To know the amount of CO₂ that is absorbed in 8 mL absorbent, can be determined by determining the total karbon. Perhitungan total carbon can be found in appendix 4. The number of CO₂ is successfully absorbed 1,709 g while the total of carbon present in a sample of 0.09322 g. DEA capability as an absorbent to absorb CO₂ gas can be determined by calculating the efficiency of absorption through the calculation shown in Appendix 5. Based on the results of these calculations obtained by the DEA absorption efficiency of 62.236%.

Sample enumeration Coral Reef

Liquid Scintillation Counter (LSC) Hidex 300 SL was instrumental in detecting β particles emitted from the



sample ^{14}C . Samples containing radionuclides in liquid scintillation counting method is dissolved or suspended in a solution of scintillator (Scintillator solution or cocktail) that fits inside the glass or plastic vial. Scintillator material is a material that would emit photons when radiation interacts with the particles. In the enumeration process takes 8 mL of sample and 12 mL of scintillator were mixed into a 20 mL vial. The process of mixing the sample solution and the scintillator, avoiding contamination by free air containing CO_2 -free. Enumeration with LSC Hidex 300 SL carried out over a period of 1-240 minutes. Analysis of the samples by this method involves a scintillator solution that will collide with the excited molecules to the solvent. At this point the energy will be released in the form of photons or light flicker. Flicker of light has a certain wavelength and when it reaches the layer fotokatode in PMT (Photo Multiplier Tube) releases electrons from the layer. The electrons will be reproduced by dinode-dinode contained in PMT and eventually these electrons will be collected at this anode in the form of electrical pulses. A sample census carried out in two phases, phase optimum time determination enumeration and the stage of determining the value of the average value of enumeration sample at the optimum time. The following data is the result of the determination of the optimum time of enumeration of activity ^{14}C contained in the sample can be seen in Table 2.

According to the table 2 can be seen enumeration results on samples of coral reefs from the 15th minute until the 60th minute decline.

Table 2. Results of Enumeration Data for Determining Optimum Time Shredded samples Barrang Lompo Island Coral Reef Spermonde Island with LSC Device Hidex 300 SL in the time range of counts from 1-150 minutes.

Sampel				
Shredded				
No.	Time (Minutes)	CPM	DPM	TDCR
1.	5	55,600	100,370	0,553
2.	15	61,660	105,830	0,582
3.	30	58,130	99,100	0,586
4.	60	58,630	98,880	0,592
5.	90	58,120	98,650	0,589
6.	120	57,270	97,600	0,586
7.	150	57,380	97,370	0,589

But in the 90th minute of ^{14}C activity values ranging achieve stability. ^{14}C activity value which fluctuates due to the effects of chemical glow (chemiluminescence) when counting takes place and the instability of the phase between the scintillator carbamate solution at the beginning of the process of enumeration. Phase instability caused by the effects of the blackout (quenching). Blackout effect is a shift in the fluorescence spectrum toward lower energy. The greater the blackout happened, then the fluorescence spectrum increasingly towards lower energy. CPM impairment occurs because the number of nuclei decay during certain time intervals decreased exponentially. The decline in the value of CPM a sample proportional to the decline in value of DPM but inversely proportional to the value TDCR samples. If made in the form of graphs, the ratio

between the CPM and DPM of the time it will look like in figure 3.

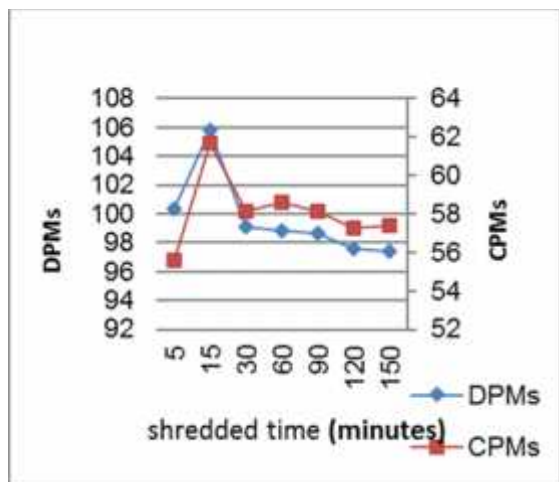


Figure 3. Graph relations DPM and CPM sample results reefs against time

Determining the optimum time to determine enumeration best time value produced DPM and have efficient value enumeration (TDCR) stable as a sign that the sample enumeration process walk up. In the minutes to 30-90 value of the activity of ^{14}C begin to achieve stability. The cause is physical and chemical conditions sample solution with scintillator is stabilized. ^{14}C activity rate stability is essential to gain an exponential graph chopped. From the table it obtained a sample of enumeration optimum for 90 minutes, with a value of 98.650 DPM, CPM at 58.120 and TDCR value of 0.589. the samples then enumerated repeatedly during the optimum time. The results of the count at the optimum time is used to calculate the specific activity of ^{14}C in the sample. The following data enumeration results samples at the time of enumeration optimum for 90 minutes with 5 repetitions can be seen in Table 3.

Table 3. Data from sample enumeration Barrang Island Coral Reef Islands Lompo Spermonde with LSC Device Hidex 300 SL at the optimum time of enumeration for 90 minutes with 5 repetitions.

Sample				
Shredded				
No.	Time (Minutes)	CPM	DPM	TDCR
1.	90	58,830	98,670	0,596
2.	90	58,500	99,220	0,589
3.	90	58,570	99,870	0,586
4.	90	61,060	101,840	0,599
5.	90	59,460	99,740	0,596
Mean		59,284	99,868	0,5932

Table 4. The enumeration results Data for Determination of Optimum Time Shredded Background with LSC device Hidex 300 SL in a span of chopped 5-240 minutes.

Background				
shredded				
No.	time (minutes)	CPM	DPM	TDCR
1.	5	64,400	115,200	0,559
2.	15	62,330	109,760	0,567
3.	30	60,060	102,590	0,585
4.	60	59,130	102,990	0,574
5.	90	57,030	99,440	0,573
6.	120	57,250	97,930	0,584
7.	150	57,180	98,060	0,583
8.	180	57,360	100,710	0,569
9.	210	56,040	95,640	0,585
10.	240	56,910	97,310	0,584

Optimum background count values from the table above that the shredded for 90 minutes. Values obtained at the time of

enumeration for 90 minutes is a value CPM background amounted to 57.030 values DPM optimum amounted to 99.440 and the value TDCR optimum at 0.573. These results are then used to determine the average value of the background activity at the time of enumeration optimum 90 minutes. Results chopped background when made into shape of the graph will look like Figure 4.

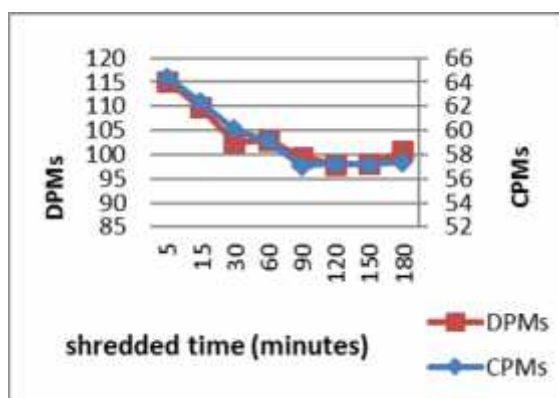


Figure 4. Graph relationship results DPM and CPM background against time.

The data is the average value of the background activity at the time of enumeration optimum 90 minutes can be seen in Table 4.

Table 4. Data average value of background activity by LSC Device Hidex 300 SL at the optimum time of enumeration for 90 minutes.

Background				
No.	shredded time (minutes)	CPM	DPM	TDCR
1.	90	56,540	99,460	0,568
2.	90	57,520	99,790	0,576
3.	90	56,880	98,370	0,578
4.	90	56,450	99,010	0,570
5.	90	56,830	99,010	0,573
mean		56,844	99,128	0,573

Background enumeration is done to get the value of Disintegrations Per Minute (DPM) ^{14}C in samples obtained based on the difference of the value of DPM sample and DPM background value. The use of the results of the background enumeration herein is intended to find out the contribution of radiation from liquid scintillation counting environments that are not sampled. As described earlier, the results of the background chopped also be used as a correction factor to the count samples.

Data analysis Determination of Specific Activity Sample Coral Reef.

The specific activity of samples of coral reefs can be determined from the range of the result of chopped *Counts Per Minute* (CPM) samples against the result of enumeration background generated as a correction factor to the results of chopped samples divided by the efficiency of the enumeration *Triple To Double Coincidence Ratio* (TDCR) are converted into units of *Disintegration Per Minute* (DPM), divided by the total levels of carbon in 8 mL of sample was mixed with 12 mL of scintillator. From the explanation to do the determination of the specific activity of the sample. The specific activity of the average (US) samples from the calculation of disintegrations per minute (DPM) per unit carbon future samples can be seen in Table 5.

Table 5. The average ^{14}C Sample Originally Island Coral Reef Barrang Lompo Island Spermonde Island.

Sample	DPM	C-total (g)	As (DPM/gC)	AS ^{14}C life*
Coral reefs	1,709	0,09322	7,938192	15,3



Based on data from a sample census results in Table 5, shown specific activity of ^{14}C in samples 7,938192 dpm/gC. Calculation of the sample activity coral reefs can be seen in appendix. Activities obtained indicates the magnitude of the decay of carbon atoms that takes place every minute (DPM) in one gram of carbon.

The Calculation of Coral Reef Age

Age samples of coral reefs can be determined by comparing the value of the specific activity of modern carbon (15.3 dpm/GRC) with a specific activity of samples obtained using radiocarbon decay rate equation:

$$t = \frac{t_{1/2}}{\ln 2} \ln \frac{A_0}{A}$$

Information :

A = radioactivity isotope ^{14}C in the sample
 A_0 = radioactivity isotope ^{14}C at the time of the plant or animal life (15.3 dpm/gC) (Libby, 1960)

$t_{1/2}$ = half-life = 5730 years

$\ln 2 = 0.693$.

From these equations, the age of the samples of coral reefs Barrang Lompo Island Spermonde Island can be seen in Table 6.

Table 6. Data Calculation Results of Coral Reef Age

Sample	Age (Year)
Coral reefs	5425,452

4.CONCLUSION

Based on the research that has been done can be concluded that:

1. Efficiency (%) diethanolamine (DEA) as absorbents in the pre-treatment of the

sample in the analysis of ^{14}C coral reefs in Barrang Lompo Island is 62.236%.

2.The age of coral reefs from the Barrang Lompo island, Spermonde Islands which is calculated based on the equation of radiocarbon decay rate is 5425.452 year.

REFERENCES

- [1] Aulia, K.N., Kasmara, H., Erawan, T.S., Natsir, S.M., 2012, Kondisi Perairan Terumbu Karang Dengan Foraminifera Bentik Sebagai Bioindikator Berdasarkan *Foram Index* Di Kepulauan Banggai, Provinsi Sulawesi Tengah, *Jurnal Ilmu dan Teknologi Kelautan Tropis*, Jakarta, **4** (2): 335-345.
- [2] Boekschoten, G. J. dan Best, M. B., 1988, Fossil and Recent Shallow Water Corals from The Atlantic Islands Off Western Africa, *Life and Marine Science Journal* ,**68** (2): 99-112.
- [3] Faure, G., 1986, *Principle of Isotope Geology*: 386-404.
- [4] Kim, E.Y., Lim,J.A., Jeong, S.K., Yoon, Y. I., Bae, S.T., and Nam, S.C., 2013, Comparison of Carbon Dioxide Absorption in Aqueous MEA, DEA, TEA, and AMP Solutions, *Bull. Korean Chem. Soc.*, **34** (3), 783-787.
- [5] Kim, S. dan Kim, H.T., 2004, Aspen Simulation Of CO_2 Absorption System With Various Amine Solution, Dept. of Energy Studies, Ajou University, Korea, **49** (1).
- [6] Lasabuda, R., 2013, Pembangunan Wilayah Pesisir Dan Lautan dalam Perspektif Negara Kepulauan Republik Indonesia, *Jurnal Ilmiah Platax*, FPIK UNSRAT, **1** (2): 92-101.



- [7] Libby, W.F., 1960, Radiocarbon Dating, *Nobel Lecture*, Elsevier Publishing Company, Amsterdam.
- [8] Manapa, E., 2011, Profil Dunia Kelautan Dalam Perspektif Siswa Indonesia di Tingkat Sekolah Dasar, *Jurnal Penelitian Pendidikan*, UPI, **11** (1): 66-74.
- [9] Pratikno, B., Abidin, Z., Sidauruk, P., dan Satrio, 2009, Aplikasi Isotop Alam ^{18}O , ^2H dan ^{14}C untuk Studi Air Tanah di Kepulauan Seribu, *Jurnal Ilmiah Aplikasi Isotop dan Radiasi*, Pusat Aplikasi Teknologi Isotop dan Radiasi, Badan Tenaga Nuklir Nasional, Jakarta, **5** (1): 68-82.
- [10] Sumarjitho, 2011, *Spermonde Archipelago; Sulawesi Selatan*, (Online), (<http://sumarjitho.blogspot.com/2011/12/kepulauan-speronde-sulawesi-selatan.html>), diakses pada tanggal 22 Maret 2014).
- [11] Tjahaja, I.P., dan Mutiah, 2000, Metode Pencacahan Sintilasi Cair : Salah Satu Alternatif untuk Pengukuran α dan β Total dalam Sampel Lingkungan, *Indonesian Journal of Nuclear Science and Technology*, **1** (1) : 31-46.
- [12] Yuliati, H. dan Akhadi, M., 2005, *Radionuklida Kosmogenik Untuk Penanggalan*, Puslitbang Keselamatan Radiasi dan Biomedika Nuklir, Buletin Alara, **6** (3): 163-171.